

on each metal atom and the upper A-type  $\pi$  orbital of the RNCCNR group,  $\psi_3$ , are permitted by symmetry to interact as shown in Figure 2 to give three MO's, one of which,  $\psi_b$ , will be a good bonding orbital for the  $M(1)C_2N_2R_2M(2)$  system as a whole. There will also be a corresponding antibonding MO,  $\psi_a$ , and an essentially nonbonding MO,  $\psi_n$ , made up of the two metal  $d\pi$  orbitals only.

When these metal-ligand interactions are considered in conjunction with the other  $\pi$  orbitals of the bridging butadiene ligand and the  $d\pi$  orbitals that are orthogonal to the  $C_2N_2R_2$   $\pi$  orbitals, we get the picture shown in Figure 3. It can be seen that the interaction of the two sets of  $\pi$  orbitals leads to the formation of a singlet  $\pi^6$  configuration and accounts for the diamagnetism of the molecule. There is a symmetry-permitted interaction between the  $\psi_n$  orbital of Figure 2 and the  $\psi_1$  MO of the  $C_2N_2R_2$  group which leads to a slight mixing and a slightly increased separation of these orbitals; they are thus shown slightly displaced and are designated  $\psi_n'$  and  $\psi_1'$  in Figure 3.

**Concluding Remarks.** Returning again to the question of how these unusual molecules are formed, we do not have any detailed idea. It is significant that the same sort of product can be obtained for both niobium and tantalum. Although transition metals are known to catalyze polymerization<sup>12</sup> of isocyanides this complex-mediated dimerization appears to be unprecedented.<sup>12,15,16</sup> One

prior example of such coupling has been reported but under explicitly reductive conditions in the presence of zinc giving  $\eta^2$ -RHNCNHR bonded to Mo.<sup>17</sup> It is possible that in our case the crucial factor is the presence of the double bonded  $M=M$  unit. The same number of chlorine atoms in both the starting complex and the resulting product as well as the high efficiency of the process indicate that the dinuclear unit may not be cleaved into separate mononuclear species. The participation of monomeric intermediates would be expected to give more heterogeneous products.

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**Registry No.**  $Nb_2Cl_6(t-BuNC)_6$ , 85533-79-5;  $Nb_2Cl_6(CyNC)_6$ , 92078-20-1;  $Nb_2Cl_6(i-PrNC)_6$ , 92078-21-2;  $Ta_2Cl_6(i-PrNC)_6$ , 92078-19-8;  $Nb_2Cl_6(SMe_2)_3$ , 61069-51-0;  $Ta_2Cl_6(SMe_2)_3$ , 77827-59-9.

**Supplementary Material Available:** Tables of observed and calculated structure factors, anisotropic thermal parameters,  $B$ 's, complete listing of bond distances and angles, and selected least-squares planes (40 pages). Ordering information is given on any current masthead.

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## N,O-Silatropic Rearrangements. Enhanced Silyl Group Exchange between Nitrogen and Oxygen via Chelation to Nickel and X-ray Crystal Structure of a Substituted N,O-Disilylimidate Moiety

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**Abstract:** The nickel(II) hydrocarbyl complexes  $Ni(R)[N(SiMe_2CH_2PPh_2)_2]$  ( $R$  = methyl, allyl, vinyl, and phenyl) react with 1 atm of carbon monoxide at room temperature to generate nickel(0) dicarbonyl derivatives  $Ni(CO)_2[RC=N-(SiMe_2CH_2PPh_2)OSiMe_2CH_2PPh_2]$ . Loss of one CO ligand from the vinyl derivative  $Ni(CO)_2[C_2H_3C=N-(SiMe_2CH_2PPh_2)OSiMe_2CH_2PPh_2]$  occurs readily under vacuum to produce a new Ni(0) complex containing an  $\eta^2$ -bonded acryloyl unit. This species,  $Ni(CO)[(\eta^2-C_2H_3)C=N(SiMe_2CH_2PPh_2)OSiMe_2CH_2PPh_2]$ , has been structurally characterized by X-ray crystallography: space group  $P2_1/n$ ;  $a = 16.240$  (3) Å,  $b = 11.534$  (1) Å,  $c = 19.076$  (3) Å;  $Z = 4$ ;  $R = 0.050$ ,  $R_w = 0.058$ . The exclusive N,O-disilylimidate tautomeric form of the diphosphine ligand in all of these complexes was established spectroscopically through <sup>15</sup>N labeling and variable-temperature <sup>1</sup>H and <sup>29</sup>Si NMR experiments. Rapid silyl group exchange between the nitrogen and oxygen centers occurs with all of these Ni(0) complexes. In fact, comparison of  $\Delta G^\ddagger$  values for silyl exchange for the uncoordinated acylated disilylphosphine  $PhC=N(SiMe_2CH_2PPh_2)OSiMe_2CH_2PPh_2$  and its Ni(0) derivative indicate a substantial enhancement for this migration when the ligand is bound to Ni; the reason for the enhancement in the rate of silyl group migration is discussed.

### Introduction

It has been well documented<sup>2-4</sup> that, except in the case of  $HCON(SiMe_3)_2$ , all linear bis(trimethylsilyl)amides,  $RCON-$

$(SiMe_3)_2$  ( $R$  = alkyl or aryl), exist predominantly as the N,O-disilylimidate tautomer **1** rather than as the amide isomer **2**. In addition, all alkyl and aryl amides undergo reversible intramolecular exchange of the trimethylsilyl groups between the nitrogen and oxygen centers. It is generally accepted<sup>3-5</sup> that the mechanism of this silyltropic rearrangement involves rapid, free rotation of

(1) Fellow of the Alfred P. Sloan Foundation, 1984-1986.

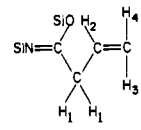
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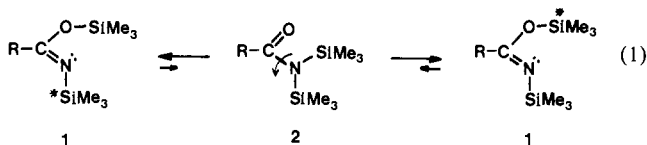
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Table I.  $^1\text{H}$  NMR Data<sup>a</sup>

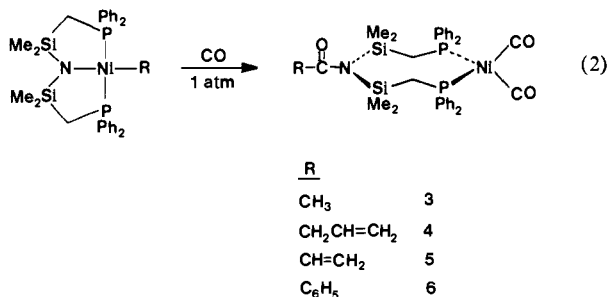
	SiCH <sub>3</sub>	CH <sub>2</sub> P	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> P	other	
$\text{Ni}(\text{CO})_2[\text{CH}_3\text{C}=\text{N}-\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{O}-\text{SiMe}_2\text{CH}_2\text{PPh}_2]$	-0.11 (s)	1.89 (br d)	6.95 (m, para/meta)	CNCH <sub>3</sub> 1.91 (s)	
$\text{Ni}(\text{CO})_2[\text{C}_3\text{H}_5\text{C}=\text{N}-\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{O}-\text{SiMe}_2\text{CH}_2\text{PPh}_2]$	-0.10 (s)	1.89 (br d)	6.95 (m, para/meta)	7.53 (m, ortho)	
					H <sub>1</sub> , 3.08 (dt, 2, J <sub>1,2</sub> = 6.59, J <sub>1,3</sub> = J <sub>1,4</sub> = 1.46)
			7.52 (m, ortho)	H <sub>2</sub> , 5.85 (m, 1, J <sub>2,4</sub> = 10.01, J <sub>2,3</sub> = 17.09)	
				H <sub>3</sub> , 5.02 (m, 1, J <sub>3,4</sub> = 1.71)	
				H <sub>4</sub> , 4.85 (m, 1)	
$\text{Ni}(\text{CO})_2[\text{C}_2\text{H}_5\text{C}=\text{N}-\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{O}-\text{SiMe}_2\text{CH}_2\text{PPh}_2]$	-0.08 (s)	1.85 (br m)	6.95 (m, para/meta)	H <sub>1</sub> , 6.17 (dd, J <sub>1,3</sub> = 17.0, J <sub>1,2</sub> = 2.0)	
			7.15 (m, ortho)	H <sub>2</sub> , 5.38 (dd, J <sub>2,3</sub> = 10.2)	
				H <sub>3</sub> , 5.99 (dd)	
$\text{Ni}(\text{CO})[(\eta^2\text{-C}_2\text{H}_5)\text{C}=\text{N}-\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{O}-\text{SiMe}_2\text{CH}_2\text{PPh}_2]$	-0.65 (s)	0.82 (dd, J <sub>H,P</sub> = 7.0, J <sub>gem</sub> = 10.5)	6.70, 6.98 (m, para/meta)	H <sub>1</sub> , 4.34 (m, J <sub>1,3</sub> = 11.72, J <sub>1,P1</sub> = 6.59, J <sub>1,P2</sub> = 1.46)	
	-0.35 (s)		7.48, 7.92 (m, ortho)		
	0.35 (d, <sup>4</sup> J <sub>H,P</sub> = 0.98)	1.08 (dd, J <sub>H,P</sub> = 13.0, J <sub>gem</sub> = 12.0)		H <sub>2</sub> , 3.89 (m, J <sub>2,3</sub> = 7.57, J <sub>2,P1</sub> = 5.62, J <sub>2,P2</sub> = 4.15)	
	0.65 (d, <sup>4</sup> J <sub>H,P</sub> = 0.98)	1.46 (dd, J <sub>H,P</sub> = 15.0, J <sub>gem</sub> = 12.0)		H <sub>3</sub> , 4.14 (m, J <sub>3,P1</sub> = 13.92, J <sub>3,P2</sub> = 3.17)	
		1.69 (dd, J <sub>H,P</sub> = 6.0, J <sub>gem</sub> = 10.5)			
$\text{Ni}(\text{CO})_2[\text{C}_6\text{H}_5\text{C}=\text{N}-\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{O}-\text{SiMe}_2\text{CH}_2\text{PPh}_2]$	0.03	1.93 (br m)	6.92 (m, para/meta)	CNC <sub>6</sub> H <sub>5</sub> 6.92 (m)	
			7.52 (m, ortho)		
$\text{C}_6\text{H}_5\text{C}=\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{OSiMe}_2\text{CH}_2\text{PPh}_2$	0.24 (s)	1.68 (s)	7.10 (m, para/meta)	CNC <sub>6</sub> H <sub>5</sub> 7.50 (m), 8.03 (m)	
	0.48 (s)	1.93 (s)	7.51 (m, ortho)		

<sup>a</sup> In  $\delta$  ( $J$  values in hertz).

the carbon-nitrogen bond in the *N,N*-disilylamide tautomer **2** as depicted in eq 1.

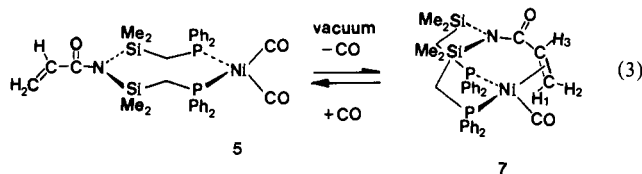


In a previous communication,<sup>6</sup> we reported an unusual carbon monoxide promoted, ligand rearrangement of several nickel(II) alkyl and aryl complexes to generate nickel(0) products (eq 2)

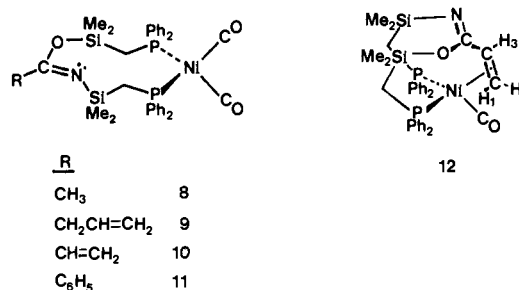


which contained, as part of the backbone of the ligand, the *N,N*-

*N,N*-disilylamide moiety (cf. **2** in eq 1). We also discovered that the acryloyl complex **5** reversibly lost carbon monoxide to generate the  $\eta^2$ -acryloyl derivative **7** which has a nickel-olefin bond (eq 3).



We had anticipated that these complexes might undergo this amide-to-imidate tautomerism (eq 1), as observed for linear disilyl-substituted amides, but on the basis of spectroscopic evidence (vide infra), this possibility was initially discounted. However, recent X-ray structural data for purported **7**, in addition to <sup>15</sup>N-labeling studies, variable-temperature <sup>1</sup>H NMR and <sup>29</sup>Si NMR results, have indicated that all of these nickel(0) derivatives **3-7** exist, both in solution and in the solid state, predominantly as the imidate isomers **8-12**, respectively.



(6) (a) Fryzuk, M. D.; MacNeil, P. A. *Organometallics* **1982**, *1*, 1540-1541. (b) We previously reported<sup>6a</sup> that the reaction of Ni(C<sub>6</sub>H<sub>5</sub>)[N(SiMe<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] with CO for seven hours yielded a mixture of two products: the Ni(II) benzoyl derivative Ni(COC<sub>6</sub>H<sub>5</sub>)[N(SiMe<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>] and the Ni(0) product Ni(CO)<sub>2</sub>[(C<sub>6</sub>H<sub>5</sub>)C=N(SiMe<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>OSiMe<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>]. As will be reported in due course, the Ni(II) benzoyl complex can be prepared exclusively by using a shorter reaction time (1 h).

Herein we describe full details of this work as well as a discussion of the influence of the nickel center on the rate of the silyl group exchange process.

### Experimental Section

**General Procedure.** The preparation of all compounds was carried out by using standard techniques and equipment for handling air- and moisture-sensitive materials as previously described.<sup>7</sup> The synthesis of the nickel(II) alkyl and aryl complexes  $[\text{Ni}(\text{R})\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$  (R = methyl, allyl, vinyl, phenyl) was carried out via metathesis of  $[\text{NiClN}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$  with the appropriate freshly prepared Grignard reagent, as described in ref 7. All spectra were recorded in  $\text{C}_6\text{D}_6$  or  $\text{C}_7\text{D}_8$  at room temperature (unless otherwise indicated). Chemical shifts are in parts per million with the coupling constants expressed in hertz (Table I);  $^1\text{H}$  NMR chemical shift values are referenced to  $\text{C}_6\text{D}_5\text{H}$  at 7.15 ppm;  $^{31}\text{P}$  chemical shifts are referenced to  $\text{P}(\text{OMe})_3$  at 141.0 ppm;  $^{29}\text{Si}$  values are with respect to  $(\text{Me}_3\text{Si})_2\text{O}$  at 0 ppm; the standard for  $^{15}\text{N}$  spectra is  $\text{CH}_3\text{NO}_2$  at 0 ppm;  $^{13}\text{C}$  spectra are referenced to  $\text{Me}_4\text{Si}$  at 0 ppm.

$\text{C}_6\text{H}_5\text{C}\equiv\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{OSiMe}_2\text{CH}_2\text{PPh}_2$ . To a cold ( $-78^\circ\text{C}$ ) solution of  $\text{LiN}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2$  (1.07 g, 2 mmol) in toluene (100 mL) was slowly added a solution of benzoyl chloride (0.28 g, 2 mmol) in toluene (10 mL) with stirring. After the solution was warmed to room temperature, the solvent was removed in vacuo and the residue extracted with hexanes, filtered through Celite, and pumped down to a colorless oil. Attempts to crystallize the product were unsuccessful: IR (hexanes)  $\nu_{\text{C}=\text{N}} = 1695$  (s)  $\text{cm}^{-1}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta -23.36$  (s),  $-23.66$  (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\text{C}=\text{N}$ ,  $\delta 159.1$  (s);  $^{29}\text{Si}\{^1\text{H}\}$  (inverse-gated) NMR  $\text{SiN}=\text{C}$ ,  $-14.77$  (d,  $J_{\text{P,Si}} = 17.1$  Hz),  $\text{SiOC}$ ,  $10.07$  (d,  $J_{\text{P,Si}} = 17.1$  Hz).

**$^{15}\text{N}$ -Labeled Compounds.**  $^{15}\text{NH}_4\text{Cl}$  (99 atom %  $^{15}\text{N}$ ) was obtained from Merck, Sharpe, Dohme and dried at  $120^\circ\text{C}$  for 24 h prior to use.

$(\text{ClCH}_2\text{SiMe}_2)_2^{15}\text{NH}$ . The following preparation was carried out in a 250-mL heavy-walled flask fitted with a Kontes 9-mm needle-valve inlet. To a suspension of finely crushed  $^{15}\text{NH}_4\text{Cl}$  (1.09 g, 0.02 mol) in THF (100 mL) was added  $\text{ClCH}_2\text{SiMe}_2\text{Cl}$  (5.7 g, 0.04 mol). The mixture was cooled to  $0^\circ\text{C}$ . Triethylamine (6.1 g, 0.06 mol) was added, the flask was sealed, and the suspension was then stirred vigorously at room temperature for 7 days. The solvent was removed in vacuo and the product extracted with hexanes, filtered, and pumped down. Distillation of the resultant yellowish oil (bp  $103^\circ\text{C}$  (10 mm)) gave the product in  $\sim 80\%$  yield as a clear, colorless liquid.

The distilled  $^{15}\text{N}$ -labeled 1,3-bis(chloromethyl)tetramethyldisilazane was then reacted with 2 equiv of  $\text{LiPPh}_2$  to form  $\text{H}^{15}\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2$ , as previously described for its  $^{14}\text{N}$  analogue.<sup>7</sup> Similarly,  $\text{Li}^{15}\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2$ ,  $[\text{NiCl}^{15}\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$ , and  $[\text{Ni}(\text{R})^{15}\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$  were prepared via synthetic routes previously outlined for their  $^{14}\text{N}$  isotopomers.

**Carbonylation Reactions.** All reactions of the Ni(II) alkyls with CO and  $^{13}\text{CO}$  to produce the Ni(0) derivatives  $[\text{Ni}(\text{CO})_2\text{RC}\equiv\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{OSiMe}_2\text{CH}_2\text{PPh}_2]$  were performed<sup>6b</sup> at 1 atm of pressure at room temperature in toluene. Typically, 0.02 M solutions of the Ni complexes  $[\text{Ni}(\text{R})\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$  (R = methyl, allyl, vinyl, phenyl) were rapidly stirred under carbon monoxide. A typical preparation is given below.

$[\text{Ni}(\text{CO})_2\text{CH}_2\text{C}\equiv\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{OSiMe}_2\text{CH}_2\text{PPh}_2]$ . A solution of  $[\text{Ni}(\text{CH}_3)\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$  (0.12 g, 0.20 mmol) in toluene (10 mL) was stirred under 1 atm of carbon monoxide at room temperature. Within 5 min, the original gold-orange faded to a clear, colorless solution. The solvent was removed in vacuo and the resultant oil taken up in minimum hexanes. Colorless crystalline clusters of needles were filtered and washed with cold hexanes: yield 0.12 g (85%); mp  $122^\circ\text{C}$ ; mol wt (Signer), theoretical 689, found 698; IR (KBr)  $\nu_{\text{CO}}$  1990 (vs), 1930 (vs),  $\nu_{\text{C}=\text{N}}$  1705 (s)  $\text{cm}^{-1}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta 15.10$  (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\text{C}=\text{N}$ ,  $\delta 161.9$  (s),  $\text{NiCO}$ , 200.2 (t,  $J_{\text{Ni,C}} = 2.4$  Hz);  $^{15}\text{N}\{^1\text{H}\}$  NMR (inverse-gated)  $\delta -140.8$  (s);  $^{29}\text{Si}\{^1\text{H}\}$  NMR (inverse-gated)  $\delta -1.17$  (s). Anal. Calcd for  $\text{C}_{34}\text{H}_{39}\text{NNiO}_3\text{P}_2\text{Si}_2$ : C, 59.48; H, 5.68; N, 2.04. Found: C, 59.30; H, 5.73; N, 1.80.

$[\text{Ni}(\text{CO})_2\text{C}_2\text{H}_5\text{C}\equiv\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{OSiMe}_2\text{CH}_2\text{PPh}_2]$ . The synthesis of this complex was carried out in an identical manner as outlined for its acetyl analogue: yield 80%; mp  $138-140^\circ\text{C}$ . IR (KBr)  $\nu_{\text{CO}}$  1985 (vs), 1925 (vs),  $\nu_{\text{C}=\text{N}}$  1685 (s)  $\text{cm}^{-1}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta 14.65$  (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\text{C}=\text{N}$ ,  $\delta 162.4$  (s),  $\text{NiCO}$ , 200.9 (s). Anal. Calcd for  $\text{C}_{36}\text{H}_{41}\text{NNiO}_3\text{P}_2\text{Si}_2$ : C, 60.67; H, 5.76; N, 1.97. Found: C, 60.66; H, 5.89; N, 1.80.

Table II. Crystallographic data for

$[\text{Ni}(\text{CO})\{(\eta^2\text{-CH}=\text{CH}_2)\text{C}\equiv\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{OSiMe}_2\text{CH}_2\text{PPh}_2\}]^a$	
formula	$\text{C}_{34}\text{H}_{39}\text{NNiO}_3\text{P}_2\text{Si}_2$
fw	670.52
cryst system	monoclinic
a, Å	16.240 (3)
b, Å	11.534 (1)
c, Å	19.076 (3)
$\beta$ , deg	105.392 (7)
V, Å <sup>3</sup>	3444.9 (9)
Z	4
$D_{\text{calcd}}$ , g/cm <sup>3</sup>	1.293
space group	$P2_1/n$
$F(000)$	1408
bounding planes <sup>b</sup>	$\pm(-1,1,0)$ , $0.088$ , $\pm(110)$ , $0.060$ , $\pm(1,-1,1)$ , $0.175$ , $\pm(001)$ , $0.263$
$\mu(\text{Mo K}\alpha)$ , cm <sup>-1</sup>	7.54
transmission factors	0.864-0.917
diffractometer	Enraf-Nanius CAD4-F
scan type	$\omega-2\theta$
scan speed, deg/min	0.80-6.71
scan range, deg in $\omega$	$0.65 + 0.35 \tan \theta$
data collected	$\pm h, +k, +l$
$2\theta$ max, deg	48
no. of unique reflctns	5089
reflctns with $I \geq 3\sigma(I)$	1733
no. of variables	391
$R(\text{obsd reflctns})$	0.050
$R_w(\text{obsd reflctns})$	0.058
goodness of fit	2.119

<sup>a</sup> Temperature =  $22^\circ\text{C}$ ; Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å); graphite monochromator; takeoff angle =  $2.7^\circ$ ; aperture  $(2.0 + \tan \theta) \times 4.0$  mm at a distance of 173 mm from the crystal; scan range extended by 25% on both sides for background count;  $\sigma^2(I) = S + 2B + [0.04(S - B)]^2$  ( $S$  = scan count,  $B$  = normalized background count); function minimized  $\sum w(|F_o| - |F_c|)^2$  where  $w = 1/\sigma^2(F)$ ,  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ , and  $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$ . <sup>b</sup> Followed by distances in mm from a common origin.

$[\text{Ni}(\text{CO})_2\text{C}_2\text{H}_5\text{C}\equiv\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{OSiMe}_2\text{CH}_2\text{PPh}_2]$ . Upon stirring a toluene solution of  $\text{Ni}(\eta^2\text{-CH}=\text{CH}_2)\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2$  under CO for 3 h, followed by rapid removal of solvent under reduced pressure, a mixture of two identifiable products was obtained.  $[\text{Ni}(\text{CO})_2\text{C}_2\text{H}_5\text{C}\equiv\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{OSiMe}_2\text{CH}_2\text{PPh}_2]$  was the major product ( $\sim 90\%$ ) but has not yet been obtained analytically pure due to contamination by  $[\text{Ni}(\text{CO})\{(\eta^2\text{-C}_2\text{H}_5)\text{C}\equiv\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{OSiMe}_2\text{CH}_2\text{PPh}_2\}]$  (vide infra): IR (KBr)  $\nu_{\text{CO}}$  1990 (vs), 1930 (vs),  $\nu_{\text{C}=\text{N}}$  1685 (s)  $\text{cm}^{-1}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta 15.01$  (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\text{C}=\text{N}$ ,  $\delta 157.4$  (s),  $\text{NiCO}$ ,  $\delta 199.9$  (s);  $^{15}\text{N}\{^1\text{H}\}$  (inverse-gated) NMR  $\delta -134.58$  (s).

$[\text{Ni}(\text{CO})\{(\eta^2\text{-C}_2\text{H}_5)\text{C}\equiv\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{OSiMe}_2\text{CH}_2\text{PPh}_2\}]$ . The yield of this derivative can be increased from  $\sim 10\%$  (vide supra) to greater than 90% by the following modification. After the above reaction mixture had become colorless ( $\sim 3$  h), the excess CO was removed in vacuo and the solution stirred under partial vacuum for 7 days, gradually becoming yellow-orange in color. The solvent was then removed and the product recrystallized from hexane: mp  $131-133^\circ\text{C}$ ; IR (KBr)  $\nu_{\text{CO}}$  1960 (vs),  $\nu_{\text{C}=\text{N}}$  1620 (s)  $\text{cm}^{-1}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta 16.38$  (d,  $J_{\text{P,P}_2} = 57.4$  Hz),  $-1.38$  (d);  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\text{C}=\text{N}$ ,  $\delta 166.0$  (s),  $\text{NiCO}$ , 205.2 (dd,  $J_{\text{Ni,C}_1} = 10.9$ ,  $J_{\text{Ni,C}_2} = 6.3$  Hz);  $^{15}\text{N}\{^1\text{H}\}$  (inverse-gated) NMR  $\delta -154.9$  (s);  $^{29}\text{Si}\{^1\text{H}\}$  (inverse-gated) NMR  $\text{Si}^{15}\text{N}=\text{C}$ ,  $-13.08$  (dd,  $J_{\text{Si,P}} = 4.5$ ,  $J_{\text{Si,N,Si}} = 7.5$  Hz),  $\text{SiOC}$ , 10.19 (d,  $J_{\text{Si,P}} = 5.0$  Hz). Anal. Calcd for  $\text{C}_{34}\text{H}_{39}\text{NNiO}_3\text{P}_2\text{Si}_2$ : C, 60.89; H, 5.82; N, 2.09. Found: C, 60.86; H, 6.00; N, 1.82.

$[\text{Ni}(\text{CO})_2\text{C}_6\text{H}_5\text{C}\equiv\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2\text{OSiMe}_2\text{CH}_2\text{PPh}_2]$ . **Method 1.** Although the preparation of this derivative was as described for the acetyl analogue, it is a much slower reaction, going to completion in  $\sim 2$  days: yield 72%; mp  $158^\circ\text{C}$ ; IR (KBr)  $\nu_{\text{CO}}$  1990 (vs), 1930 (vs),  $\nu_{\text{C}=\text{N}}$  1680 (s)  $\text{cm}^{-1}$ ;  $^{31}\text{P}\{^1\text{H}\}$  NMR  $\delta 15.09$  (s);  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\text{C}=\text{N}$ ,  $\delta 158.1$  (s),  $\text{NiCO}$ , 200.2 (s);  $^{15}\text{N}\{^1\text{H}\}$  (inverse-gated) NMR  $\delta -141.0$  (s). Anal. Calcd for  $\text{C}_{39}\text{H}_{41}\text{NNiO}_3\text{P}_2\text{Si}_2$ : C, 62.57; H, 5.48; N, 1.87. Found: C, 63.00; H, 5.73; N, 1.65.

**Method 2.** To a solution of  $[\text{Ni}(\text{COD})_2]^8$  (0.28 g, 1.0 mmol) in toluene (100 mL) at  $-78^\circ\text{C}$  was slowly added a solution of  $\text{C}_6\text{H}_5\text{-}$

(7) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J.; Secco, A. S.; Trotter, J. *Organometallics* **1982**, *1*, 918-930.

(8) Otsuka, S.; Rossi, M. *J. Chem. Soc. A* **1968**, 2630-2633.

$\text{C}=\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{OSiMe}_2\text{CH}_2\text{PPh}_2$  (0.63 g, 1.0 mmol) in toluene (10 mL). The mixture was stirred at  $-78^\circ\text{C}$  for 1 h, warmed to  $0^\circ\text{C}$  for an additional hour, and then allowed to come to room temperature. The solution was then exposed to 1 atm of CO and stirred for 1 h. Removal of solvent and excess CO followed by crystallization from hexanes yielded  $[\text{Ni}(\text{CO})_2\{\text{PhC}=\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{OSiMe}_2\text{CH}_2\text{PPh}_2\}]$ : yield 0.41 g (60%).

**X-ray Crystallographic Analysis.**<sup>9</sup> Crystallographic data are given in Table II. The crystal was mounted in a general orientation, lattice constants being determined by least-squares on  $2 \sin \theta / \lambda$  values for 25 reflections ( $25 < 2\theta < 35^\circ$ ) measured with Mo  $K\alpha$  radiation ( $\lambda(K\alpha_1) = 0.70930$ ,  $\lambda(K\alpha_2) = 0.71359$  Å). The intensities of three standard reflections, measured each hour throughout the data collection, showed only small random fluctuations from their initial values. The crystal was a relatively poor scatterer of X-rays, reflections with  $2\theta > 35^\circ$  being generally unobserved. The data were collected to a limit beyond this point in order to maximize the number of observed data. Decreasing the cutoff for "observed" data to  $2\sigma$  would have resulted in only 60 more reflections.

The structure was solved by conventional heavy-atom methods, the coordinates of the Ni, P, and Si atoms being determined from the Patterson function and those of the remaining non-hydrogen atoms from subsequent difference maps.<sup>9b</sup> In the early stages of refinement the phenyl rings were refined as rigid groups and the remaining non-hydrogen atoms refined with anisotropic thermal parameters. Under these conditions  $R$  was reduced to 0.082, at which point a difference map and anomalously high thermal parameters for the atoms O(1), N, and C(9) indicated a twofold disordering of the ligand backbone. Although the entire ligand is probably subject to disorder, only the atoms O(1), N, and C(9) were resolvable. Site occupancies were estimated from relative peak heights on a Fourier map to be 0.75 and 0.25. These parameters were not refined, but their appropriateness may be judged by examination of the thermal parameters obtained for resolved pairs of atoms. In subsequent cycles of refinement all non-hydrogen atoms except the low-occupancy atoms O(16), N(6), and C(96) were refined with anisotropic thermal parameters. Hydrogen atom positions and isotropic thermal parameters were calculated ( $\text{C}-\text{H} = 0.98$  Å for tetrahedral and  $0.97$  Å for planar carbon) and included as fixed atoms, except for those associated with C(96) and C(10).

Neutral atom scattering factors and anomalous scattering corrections for Ni, P, and Si were taken from ref 10. Mean and maximum parameter shifts on the final cycle of refinement corresponded to  $0.01\sigma$  and  $0.14\sigma$ , respectively. The largest fluctuations on a final difference map were  $\pm 0.47 e \text{ \AA}^{-3}$  near the Ni atom. Final positional and equivalent isotropic thermal parameters ( $U_{\text{eq}} = Y_3 \text{ trace } U_{\text{diag}}$ ) are given in Table III. Bond lengths and angles appear in Tables IV and V (only those parameters involving the high-occupancy O(1), N, and C(9) atoms being included). Calculated coordinates and thermal parameters for H atoms, anisotropic thermal parameters, torsion angles, and observed and calculated structure factor amplitudes (Tables VI-IX) are included as supplementary material.

## Results and Discussion

**Structure of the Nickel(0) Complexes.** Carbonylation of the square-planar nickel(II) methyl derivative  $\text{NiMe}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$  occurs very rapidly ( $\sim 5$  min) at room temperature under 1 atm of CO to produce the nickel(0) derivative  $\text{Ni}(\text{CO})_2[(\text{MeCON})(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$  (3 in eq 2) in virtually quantitative yield (by  $^1\text{H}$  NMR). Recrystallization from hexanes results in the formation of small, colorless crystals (unsuitable for single-crystal X-ray analysis), which are monomeric in solution ( $\text{C}_6\text{D}_6$ ). We initially formulated this material as having the *N,N*-disilylamide moiety in the ligand backbone as in 3 because the silylmethyl protons ( $\text{SiCH}_3$ ) appear as a sharp singlet in the  $^1\text{H}$  NMR down to  $-90^\circ\text{C}$ ; by comparison, the silylmethyl protons of bis(trimethylsilyl)acetamide show up as a broad singlet at room temperature, but upon cooling to  $-20^\circ\text{C}$ , two sharp singlets are observed<sup>11</sup> in line with the *N,O*-bis(trimethylsilyl)imidate tautomer 1 ( $\text{R} = \text{Me}$ ). Also consistent with structure 3 is the infrared (KBr) spectrum, which has a strong band at  $1710 \text{ cm}^{-1}$ , which we assigned to the amide carbonyl stretching frequency, and the res-

**Table III.** Final Position (Fractional,  $\times 10^4$ ; Ni, P, and Si  $\times 10^5$ ) and Isotropic Thermal Parameters ( $U \times 10^3 \text{ \AA}^2$ ) with Estimated Standard Deviations in Parentheses<sup>a</sup> for 12

atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}}/U_{\text{iso}}$
Ni	40107 (9)	55550 (14)	25094 (8)	47
P(1)	54145 (18)	56937 (27)	27134 (15)	42
P(2)	34438 (18)	62662 (28)	13901 (16)	44
Si(1)	57494 (23)	32505 (34)	20639 (24)	74
Si(2)	31244 (26)	39555 (33)	4585 (21)	70
O(1)'	3245 (6)	3392 (9)	1296 (6)	62
O(2)	3570 (8)	7165 (10)	3517 (6)	131
N'	4702 (8)	3139 (11)	1549 (9)	63
C(1)	5949 (7)	4838 (10)	2150 (6)	58
C(2)	3562 (6)	5501 (11)	601 (5)	58
C(3)	3733 (8)	6514 (13)	3106 (7)	71
C(4)	6166 (9)	2467 (13)	2940 (8)	109
C(5)	6306 (9)	2685 (13)	1407 (8)	112
C(6)	1949 (9)	3875 (12)	136 (7)	89
C(7)	3553 (10)	3213 (14)	-200 (9)	135
C(8)	4048 (9)	3411 (10)	1792 (8)	52
C(9)'	4016 (11)	3754 (14)	2524 (11)	52
C(10)	3372 (11)	4131 (13)	2785 (10)	88
C(11)	5852 (7)	7154 (11)	2661 (7)	49
C(12)	6259 (9)	7507 (13)	2169 (8)	72
C(13)	6570 (9)	8629 (17)	2168 (10)	98
C(14)	6505 (10)	9384 (14)	2671 (13)	104
C(15)	6104 (12)	9081 (14)	3196 (10)	105
C(16)	5768 (9)	7971 (16)	3158 (8)	89
C(17)	6019 (7)	5260 (10)	3640 (6)	48
C(18)	6918 (7)	5439 (10)	3846 (7)	58
C(19)	7373 (8)	5087 (13)	4553 (8)	79
C(20)	6968 (9)	4542 (12)	5027 (7)	75
C(21)	6096 (9)	4464 (11)	4827 (6)	65
C(22)	5622 (7)	4807 (10)	4123 (7)	49
C(23)	3827 (7)	7766 (12)	1279 (7)	52
C(24)	4326 (8)	7961 (13)	805 (7)	67
C(25)	4625 (10)	9055 (18)	725 (9)	90
C(26)	4416 (12)	9925 (16)	1121 (11)	97
C(27)	3960 (11)	9730 (15)	1598 (8)	89
C(28)	3641 (8)	8645 (13)	1673 (7)	64
C(29)	2279 (7)	6520 (9)	1133 (6)	43
C(30)	1874 (9)	7119 (13)	480 (7)	80
C(31)	988 (10)	7259 (14)	302 (8)	85
C(32)	525 (8)	6822 (14)	700 (10)	84
C(33)	896 (9)	6208 (13)	1346 (9)	85
C(34)	1792 (8)	6085 (11)	1556 (7)	60
O(1b)''	4736 (19)	2936 (27)	2302 (18)	58 (9)
N(b)''	4017 (27)	3376 (27)	1139 (21)	58 (10)
C(9b)''	3345 (46)	4004 (54)	2248 (33)	69 (21)

<sup>a</sup>Primed and double-primed atoms have occupancies of 0.75 and 0.25, respectively.

**Table IV.** Bond Lengths (Å) with Estimated Standard Deviations in Parentheses for 12

Ni-P(1)	2.214 (3)	C(11)-C(12)	1.346 (15)
Ni-P(2)	2.244 (3)	C(11)-C(16)	1.37 (2)
Ni-C(3)	1.731 (15)	C(12)-C(13)	1.39 (2)
Ni-C(9)	2.08 (2)	C(13)-C(14)	1.32 (2)
Ni-C(10)	2.083 (13)	C(14)-C(15)	1.38 (2)
P(1)-C(1)	1.838 (11)	C(15)-C(16)	1.39 (2)
P(1)-C(11)	1.842 (13)	C(17)-C(18)	1.423 (13)
P(1)-C(17)	1.848 (11)	C(17)-C(22)	1.362 (13)
P(2)-C(2)	1.798 (11)	C(18)-C(19)	1.41 (2)
P(2)-C(23)	1.869 (13)	C(19)-C(20)	1.40 (2)
P(2)-C(29)	1.848 (11)	C(20)-C(21)	1.369 (15)
Si(1)-N	1.729 (14)	C(21)-C(22)	1.414 (14)
Si(1)-C(1)	1.859 (13)	C(23)-C(24)	1.385 (15)
Si(1)-C(4)	1.862 (15)	C(23)-C(28)	1.343 (15)
Si(1)-C(5)	1.847 (15)	C(24)-C(25)	1.37 (2)
Si(2)-O(1)	1.687 (11)	C(25)-C(26)	1.35 (2)
Si(2)-C(2)	1.911 (13)	C(26)-C(27)	1.34 (2)
Si(2)-C(6)	1.846 (14)	C(27)-C(28)	1.38 (2)
Si(2)-C(7)	1.806 (15)	C(29)-C(30)	1.424 (15)
O(1)-C(8)	1.393 (15)	C(29)-C(34)	1.366 (14)
O(2)-C(3)	1.164 (14)	C(30)-C(31)	1.40 (2)
N-C(8)	1.31 (2)	C(31)-C(32)	1.31 (2)
C(8)-C(9)	1.46 (2)	C(32)-C(33)	1.41 (2)
C(9)-C(10)	1.35 (2)	C(33)-C(34)	1.409 (15)

(9) (a) Data collection and refinement were carried out by Dr. S. J. Rettig of the UBC Crystal Structure Service. (b) Computer programs have been detailed in ref 7.

(10) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, 1974; Vol. IV, pp 71-102, 148-151.

(11) Measured in toluene- $d_8$  on a Bruker WP-80 (80 MHz) NMR spectrometer; see ref 2.

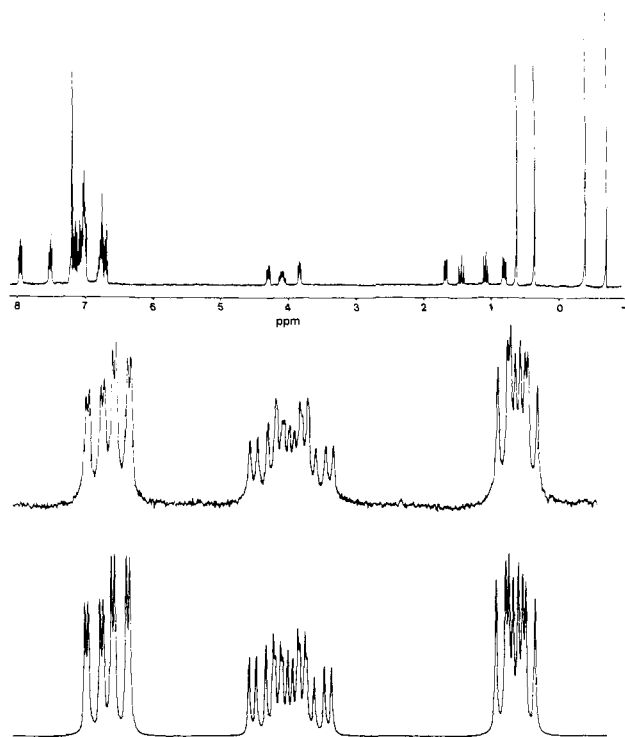
**Table V.** Bond Angles (deg) with Estimated Standard Deviations in Parentheses for **12**

P(1)-Ni-P(2)	106.50 (12)	O(1)-C(8)-N	117.2 (14)
P(1)-Ni-C(3)	105.9 (4)	O(1)-C(8)-C(9)	112.9 (14)
P(1)-Ni-C(9)	94.0 (5)	N-C(8)-C(9)	129.9 (15)
P(1)-Ni-C(10)	124.8 (5)	Ni-C(9)-C(8)	105.0 (10)
P(2)-Ni-C(3)	106.2 (4)	Ni-C(9)-C(10)	71.4 (10)
P(2)-Ni-C(9)	112.2 (5)	C(8)-C(9)-C(10)	132 (2)
P(2)-Ni-C(10)	115.0 (5)	Ni-C(10)-C(9)	70.9 (9)
C(3)-Ni-C(9)	129.1 (7)	P(1)-C(11)-C(12)	125.6 (11)
C(3)-Ni-C(10)	95.9 (6)	P(1)-C(11)-C(16)	118.7 (12)
C(9)-Ni-C(10)	37.7 (6)	C(12)-C(11)-C(16)	115.6 (13)
Ni-P(1)-C(1)	118.9 (4)	C(11)-C(12)-C(13)	121.9 (15)
Ni-P(1)-C(11)	116.8 (4)	C(12)-C(13)-C(14)	121 (2)
Ni-P(1)-C(17)	114.1 (4)	C(13)-C(14)-C(15)	120 (2)
C(1)-P(1)-C(11)	102.1 (6)	C(14)-C(15)-C(16)	117 (2)
C(1)-P(1)-C(17)	101.6 (5)	C(11)-C(16)-C(15)	124.2 (15)
C(11)-P(1)-C(17)	100.7 (5)	P(1)-C(17)-C(18)	118.1 (10)
Ni-P(2)-C(2)	120.6 (4)	P(1)-C(17)-C(22)	121.7 (9)
Ni-P(2)-C(23)	112.4 (4)	C(18)-C(17)-C(22)	120.2 (11)
Ni-P(2)-C(29)	116.3 (4)	C(17)-C(18)-C(19)	117.4 (11)
C(2)-P(2)-C(23)	104.3 (6)	C(18)-C(19)-C(20)	121.8 (11)
C(2)-P(2)-C(29)	100.7 (5)	C(19)-C(20)-C(21)	118.6 (11)
C(23)-P(2)-C(29)	99.9 (5)	C(20)-C(21)-C(22)	120.5 (11)
N-Si(1)-C(1)	104.2 (6)	C(17)-C(22)-C(21)	120.9 (11)
N-Si(1)-C(4)	122.9 (7)	P(2)-C(23)-C(24)	119.7 (12)
N-Si(1)-C(5)	100.0 (7)	P(2)-C(23)-C(28)	120.3 (11)
C(1)-Si(1)-C(4)	112.6 (6)	C(24)-C(23)-C(28)	120.0 (13)
C(1)-Si(1)-C(5)	107.6 (6)	(23)-C(24)-C(25)	120.4 (14)
C(4)-Si(1)-C(5)	108.1 (6)	C(24)-C(25)-C(26)	118.2 (15)
O(1)-Si(2)-C(2)	106.2 (5)	C(25)-C(26)-C(27)	121 (2)
O(1)-Si(2)-C(6)	98.4 (6)	C(26)-C(27)-C(28)	121.0 (15)
O(1)-Si(2)-C(7)	120.4 (7)	C(23)-C(28)-C(27)	118.8 (13)
C(2)-Si(2)-C(6)	114.0 (6)	P(2)-C(29)-C(30)	120.8 (10)
C(2)-Si(2)-C(7)	110.1 (7)	P(2)-C(29)-C(34)	119.9 (9)
C(6)-Si(2)-C(7)	107.5 (7)	C(30)-C(29)-C(34)	119.3 (11)
Si(2)-O(1)-C(8)	119.4 (9)	C(29)-C(30)-C(31)	118.4 (11)
Si(1)-N-C(8)	123.4 (13)	C(30)-C(31)-C(32)	121.9 (14)
P(1)-C(1)-Si(1)	118.8 (6)	C(31)-C(32)-C(33)	121.6 (13)
P(2)-C(2)-Si(2)	117.4 (6)	C(32)-C(33)-C(34)	118.0 (13)
Ni-C(3)-O(2)	178.1 (13)	C(29)-C(34)-C(33)	120.7 (12)

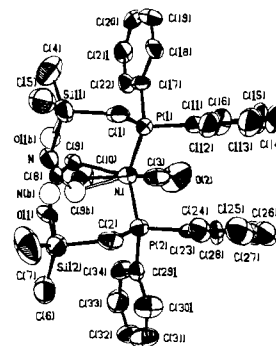
onance at 163 ppm in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum, which was assigned to the amide carbonyl carbon ( $\text{MeCONSi}_2$ ). The similarity of the spectroscopic information of the other products of CO migratory insertion with  $\text{NiR}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$  ( $\text{R} = \text{allyl, vinyl, and phenyl}$ ) led us to propose the analogous structures **4-6**. We rationalized all of the *N,N*-disilylamide tautomeric structures of **3-6** on the assumption that the 8-membered chelate ring of these ligands was preferred over the 10-membered chelate ring of complexes **7-11** formed from the *N,O*-disilylimidate moiety in the ligand backbone.

For the nickel(II) vinyl complex  $\text{Ni}(\eta^1\text{-CH}=\text{CH}_2)[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$ , the reaction with CO is complete in approximately 3 h, as evidenced by the gradual fading of the initially gold solution to completely colorless. However, the  $^1\text{H}$  NMR spectrum of the pale yellow, oily residue left after solvent removal indicated that, in addition to the expected nickel(0) dicarbonyl derivative **5** (which is the major product in  $\sim 90\%$  yield by  $^1\text{H}$  NMR), another Ni(0) species, **7**, is formed. Although **7** is a minor component of the initial product mixture, this species may be selectively separated as yellow crystals by repeated recrystallization from hexanes. In fact, attempts to obtain pure dicarbonyl **5** have been unsuccessful, since it slowly loses a CO ligand in solution under nitrogen or under vacuum to produce a species originally assigned as **7** (eq 3). The yield of **7** can be increased to  $\sim 95\%$  (by  $^1\text{H}$  NMR) by slow removal of CO under partial vacuum over a 1-week period, as indicated by the gradual deepening of the solution to a clear yellow-orange. The reversible nature of this reaction is demonstrated by the fact that yellow  $\text{C}_6\text{D}_6$  solutions of analytically pure **7**, sealed in NMR tubes under 1 atm of CO, fade to colorless within minutes; the dicarbonyl **5** is the only product.

Originally **7** was formulated, on the basis of extensive spectral data, as an  $\eta^2$ -acryloyl complex, containing one terminal carbonyl,



**Figure 1.** 400-MHz  $^1\text{H}$  NMR spectrum of **7** (see Table I for assignments) with an expanded view of the vinyl proton resonances and a computer simulation<sup>12</sup> of these multiplets.



**Figure 2.** ORTEP diagram and numbering scheme for the complex  $\text{Ni}(\text{CO})[(\eta^2\text{-C}_2\text{H}_3)\text{C}=\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)\text{OSiCH}_2\text{PPh}_2]$  (**12**) (the unshaded thermal ellipsoids represent the disorder in the backbone (see text)).

wherein the rearranged ligand binds in a tridentate fashion through the two phosphine donors as well as the  $\pi$ -system of the acryloyl moiety (eq 3). The  $^1\text{H}$  NMR spectrum of **7** is shown in Figure 1 along with an expansion of the vinyl proton resonances and a computer simulation<sup>12</sup> of these multiplets. Consistent with the purported structure for **7** are the four resonances for the silylmethyl protons due to the chirality of the  $\eta^2$ -acryloyl ligand. In addition, the resonances of the coordinated olefin are shifted upfield and split by two inequivalent (diastereotopic) phosphorus nuclei; the computer simulation in Figure 1 confirms the phosphorus couplings.

To substantiate our solution spectroscopic assignments, we subjected **7** to single-crystal X-ray analysis. The structure and numbering scheme are shown in Figure 2. There are no unusual intermolecular contacts in the solid. The geometry and disposition of donor atoms around the nickel is as predicted, that is, one terminal carbonyl along with the  $\eta^2$ -olefin and two phosphine donors; however, the backbone of the ligand has undergone a

(12) Spectral simulation was performed by using the Bruker Aspect 2000 computer system and the PANIC program (PANIC = parameter adjustment in NMR by iteration and calculation).

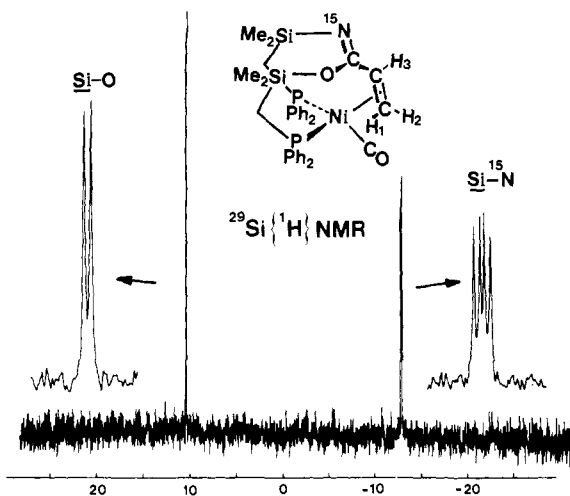


Figure 3. Inverse-gated  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum of the nickel(0)  $\eta^2$ -acryloyl complex **12**.

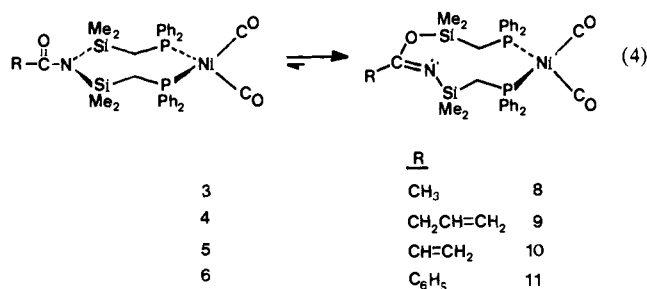
further rearrangement to generate the *N,O*-disilylimidate moiety instead of the anticipated *N,N*-disilylamide unit. It is notable that this is the first single-crystal X-ray analysis of a molecule containing a substituted *N,O*-disilylimidate fragment; the molecular structure of *N,N*-bis(trimethylsilyl)oximide bis(trimethylsilyl) ester,  $\text{Me}_3\text{SiO}(\text{Me}_3\text{Si})\text{N}=\text{C}=\text{C}=\text{N}(\text{SiMe}_3)\text{OSiMe}_3$ , is known.<sup>13</sup> The backbone of the ligand is disordered about a mirror plane which contains C(8), C(10), the nickel center, and the carbonyl ligand carbon C(3); this disorder is due to the two possible enantiomeric forms of the complex. The new formulation for **7**, represented by structure **12**, now has two chiral centers, one at C(9) and the other at the nickel center with the  $S_C, R_{\text{Ni}}$  absolute configuration (the enantiomeric  $R_C, S_{\text{Ni}}$  absolute configuration is present in the disorder). The geometry at nickel is only slightly distorted from tetrahedral with P(1)-Ni-P(2), P(1)-Ni-C(3), and P(2)-Ni-C(3) bond angles of 106.50 (12)°, 105.9 (4)°, and 106.2 (4)° respectively (Table V). The Ni-P bond lengths of 2.214 (3) and 2.244 (3) Å (Table IV) are similar to those found in other nickel complexes;<sup>7</sup> the nickel carbonyl bond length, Ni-C(3), 1.731 (15) Å, is also not unusual.

An important feature of this structure is the extended  $\pi$ -system found in the backbone of the ligand; the  $\text{SiN}=\text{CC}=\text{C}(\text{OSi})$  fragment is virtually planar in the solid state. Interestingly, molecular models of the structure shown in Figure 2, and the originally reported structure **7** indicate that in the latter form, little or no conjugation of the  $\text{O}=\text{CC}=\text{C}(\text{NSi}_2)$  fragment is possible due to the constraints of the chelating ligand's geometry. The bond angles and bond lengths in the imidate unit on the ligand are nearly identical with those found in the silylated oximide ester.<sup>13</sup>

In solution, this monocarbonyl derivative persists in the *N,O*-disilyl form on the basis of the inverse-gated  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum (Figure 3) of  $^{15}\text{N}$ -labeled **12**; a doublet ( $^2J_{\text{P}} = 5.0$  Hz) for the silicon attached to oxygen (SiOC) and a doublet of doublets ( $^2J_{\text{P}} = 4.5$  Hz,  $^1J_{\text{SiN}} = 7.5$  Hz) for the silicon attached to nitrogen-15 ( $\text{Si}^{15}\text{N}=\text{C}$ ) are observed at room temperature.<sup>14</sup> In addition, the solution infrared spectra of **12** ( $\text{CH}_2\text{Cl}_2$ , hexanes or toluene) have nearly equivalent values of  $\nu_{\text{C}=\text{N}}$  as observed in the solid-state (KBr) spectrum. Although the frequency ranges for amide vs. imidate groups overlap<sup>15</sup> in the infrared, the fact that the band at 1625  $\text{cm}^{-1}$  shifts to 1605  $\text{cm}^{-1}$  with  $^{15}\text{N}$  labeling (both KBr and solution spectra) indicates that this absorption is due to an imidate  $-\text{C}=\text{N}-$  stretch, not an amide  $\text{>C}=\text{O}$  absorption as originally reported.<sup>6</sup>

As previously mentioned, only one enantiomeric set of diastereomers ( $S_C, R_{\text{Ni}}$ ;  $R_C, S_{\text{Ni}}$ ) is observed for **12** in the solid state; this is also true in solution as evidenced by NMR ( $^1\text{H}$ ,  $^{31}\text{P}\{^1\text{H}\}$ , and  $^{29}\text{Si}$ ) where only one species is observed. Molecular models of the other possible diastereomers ( $R_C, R_{\text{Ni}}$  or  $S_C, S_{\text{Ni}}$ ) show severe steric congestion between the backbone of the ligand and the terminal carbonyl.

Having now established that **12** contained the *N,O*-disilylimidate unit in the ligand backbone, we reexamined all of the nickel(0) dicarbonyl derivatives **3-6**, which we initially assigned as having the *N,N*-disilylamide fragment in the ligand. These dicarbonyl derivatives all show bands in the amide-imidate overlap region of the infrared (KBr and solution) that shift by  $\sim 20$   $\text{cm}^{-1}$  upon  $^{15}\text{N}$  labeling, indicating that these absorptions are due to the  $-\text{C}=\text{N}-$  group of the *N,O*-disilylimidate tautomer. Therefore these complexes are reformulated as  $\text{Ni}(\text{CO})_2[\text{RC}=\text{N}-\text{Si}(\text{Me}_2\text{CH}_2\text{PPh}_2)\text{OSiMe}_2\text{CH}_2\text{PPh}_2]$  having the structures **8-11**. Further evidence for this tautomeric form for these derivatives is the absence of a band at  $980 \pm 30$   $\text{cm}^{-1}$  that has been assigned<sup>16,17</sup> to  $\nu_{\text{NSi}_2}(\text{asym})$ . Therefore the equilibrium shown in eq 4 must lie far to the right since we have been unable to detect any of the *N,N*-disilylamide tautomer.



**Enhanced Silyl Group Exchange.** The structure formulations for complexes **8-11** would appear to be in conflict with the already mentioned fact that for **8** (purported **3**), only one silylmethyl ( $\text{SiCH}_3$ ) resonance is seen in the  $^1\text{H}$  NMR spectrum (even down to  $-90$  °C). However, in the  $^1\text{H}$  NMR spectrum of **11** ( $\text{R} = \text{C}_6\text{H}_5$ ), the sharp singlet observed for the silylmethyls at ambient temperatures does broaden as the temperature is lowered to give two singlets at  $-10$  °C and further splits into four singlets at  $-90$  °C.  $\Delta G^\ddagger$  for the first process (coalescence temperature 273 K) was calculated<sup>18</sup> to be 14.9 kcal mol<sup>-1</sup> and is assigned to the silatropic rearrangement between nitrogen and oxygen; the other process (coalescence temperature  $\sim 200$  K) may be due to the freezing out of a particular conformation<sup>20</sup> of the ten-membered chelate ring of **11**. The  $^{29}\text{Si}$  NMR results also support silyl group exchange; for both  $^{15}\text{N}$ -labeled **10** and **11**, no signals were observed in the inverse-gated  $^{29}\text{Si}\{^1\text{H}\}$  NMR at ambient temperatures, consistent with an intermediate rate of exchange of the silicon nuclei on the  $^{29}\text{Si}$  NMR time scale. However, at low temperatures ( $-80$  °C), two multiplets<sup>21</sup> were observed for **11** at chemical shifts similar to those of **12**. For  $^{15}\text{N}$ -labeled **8** (for which silyl group migration could not be frozen out on the  $^1\text{H}$  NMR time scale), the inverse-gated  $^{29}\text{Si}\{^1\text{H}\}$  NMR spectrum consists of a singlet at  $-1.7$  ppm, a chemical shift which undoubtedly reflects an averaging

(16) Schirawski, Wannagat, U. *Monatsch. Chem.* **1969**, *100*, 1901.

(17) Smith, A. L. *Spectrochim. Acta* **1960**, *16*, 87.

(18)  $\Delta G^\ddagger$  for silyl group exchange was calculated by using the value for the rate constant  $k_c$  ( $k_c = \pi \Delta\nu_c/2^{1/2}$ , where  $\Delta\nu_c$ , the chemical shift separation in hertz at coalescence, is obtained by extrapolation of a plot of  $\Delta\nu$  vs. temperature to the coalescence temperature,  $T_c$ ) at the coalescence temperature<sup>19</sup> in the Eyring equation:  $\Delta G^\ddagger = -RT_c \ln(\pi \Delta\nu_c h/2^{1/2} k T_c)$  ( $R$  = gas constant;  $h$  = Planck's constant;  $k$  = Boltzmann's constant; transmission coefficient = 1).

(19) Thomas, W. A. *Annu. Rev. NMR Spectrosc.* **1968**, *1*, 43-89.

(20)  $\Delta G^\ddagger$  for this process is  $\sim 10$  kcal mol<sup>-1</sup> ( $T_c \approx 200$  K); molecular models of this 10-membered chelate ring show inequivalent silyl methyl groups for all conformations.

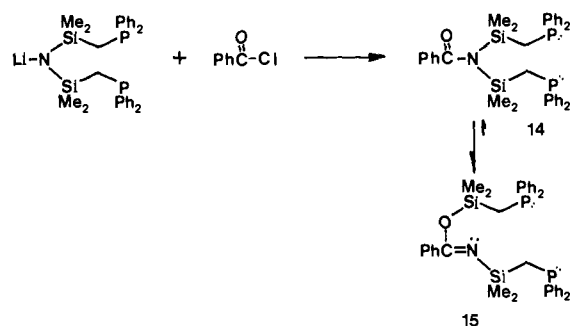
(21) Poor signal-to-noise and resolution did not allow for the determination of coupling constants.

(13) Thewalt, U.; Rinne, D. Z. *Anorg. Allg. Chem.* **1976**, *420*, 51-54.

(14) Williams, E. A.; Cargioli, J. D. *Annu. Rep. NMR Spectrosc.* **1979**, *9*, 221-318.

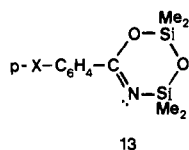
(15) "CRC Handbook of Chemistry and Physics"; Weast, R. C., Ed.; CRC Press: Cleveland, OH, 1976; Vol. 56, F237.

Scheme I

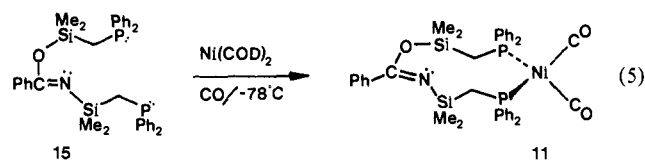


of the  $^{29}\text{Si}/^{15}\text{N}=\text{C}$  and  $^{29}\text{SiOC}$  environments<sup>22</sup> due to rapid silyl group exchange; the lack of  $^{15}\text{N}$  coupling to  $^{29}\text{Si}$  is also consistent with a rapid silatropic rearrangement.

It is remarkable, in light of the apparent ease with which this migration occurs in our cyclic nickel derivatives, that *cyclic* disilylimidates with structure **13** show no evidence for migration<sup>5</sup> of silicon groups. The  $^1\text{H}$  NMR spectrum of **13** is reported to have two singlets for the silylmethyl resonances that remain invariant in intensity and chemical shift from  $-50$  to  $+100$  °C.

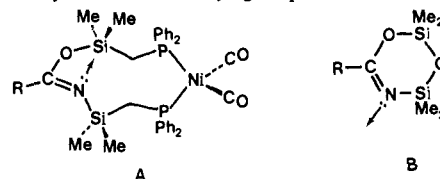


In order to accurately determine the effect of coordination to the nickel center on this silyl group exchange process, we synthesized the free diphosphine ligand **15** that contains the *N,O*-disilylimidate moiety in its backbone; the synthesis, outlined in Scheme I, follows that of the analogous trimethylsilyl derivative<sup>4</sup>  $\text{PhC}=\text{N}(\text{SiMe}_3)\text{OSiMe}_3$  and presumably proceeds via initial formation of the *N,N*-disilylamide derivative **14** that rearranges to the more stable *N,O*-disilyl tautomer. It is clear that this free ligand exists in this *N,O* form from both the  $^1\text{H}$  NMR, which shows two singlets for the silylmethyls at room temperature that coalesce as the temperature is raised to a singlet, and the  $^{29}\text{Si}$  NMR data, which show two different environments for the silicon nuclei.  $\Delta G^\ddagger$  for the exchange of silyl groups of free ligand **15** has been calculated<sup>18</sup> to be  $18.3 \text{ kcal mol}^{-1}$  ( $T_c = 343 \text{ K}$ ). By coordination of the phosphine donors of **15** to the " $\text{Ni}(\text{CO})_2$ " fragment, an enhancement of the rate of silyl group migration is observed since  $\Delta G^\ddagger$  decreases to  $14.6 \text{ kcal mol}^{-1}$  (see above) for **11**. An independent synthesis of **11** and **15** was carried out as shown in eq 5, and its spectral properties are identical with those of the genuine material produced by carbonylation of  $\text{Ni}(\text{C}_6\text{H}_5)[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$ .



(22) Bassindale, A. R.; Posner, T. B. *J. Organomet. Chem.* **1979**, *175*, 273-284.

How does chelation of the phosphine donors of **15** to a metal enhance the rate of silyl group exchange? One possibility is that the 10-membered chelate ring of **11** (and by analogy **8-10**) forces the lone pair of the imidate nitrogen atom to be in close proximity to  $\text{OSiMe}_2$  group as shown in A; this would facilitate transannular attack<sup>23</sup> to silicon by the imidate nitrogen to form the *N,N*-disilylamide intermediate. This explanation also is consistent with the fact that the cyclic imidates B ( $R = \text{aryl}$ ) do not easily exchange silyl groups since the 6-membered ring puts the nitrogen lone pair away from the *O*-silyl group.



### Conclusions

Carbonylation of nickel(II) derivatives of the formula  $\text{NiR}[\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$  ( $R = \text{CH}_3, \text{CH}=\text{CH}_2, \text{CH}_2\text{CH}=\text{CH}_2$ , and  $\text{C}_6\text{H}_5$ ) results in an unusual ligand rearrangement to produce nickel(0) derivatives in high yield that contain the *N,O*-disilylimidate moiety as part of a 10-membered chelate ring. The isomeric 8-membered chelate ring which contains the *N,N*-disilylamide fragment in the backbone was not detected but is a presumed intermediate in the silyl group exchange process.

A further ligand rearrangement occurs for the nickel dicarbonyl derivative **10** ( $R = \text{CH}=\text{CH}_2$ ) upon loss of  $\text{CO}$  under vacuum; the vinyl portion of the ligand backbone coordinates to the nickel in a completely diastereoselective fashion to generate a tridentate mode of ligation. The single-crystal X-ray structure of **12** was determined, and, for the first time, the metrical details of a substituted *N,O*-disilylimidate fragment have been ascertained.

Except for **12**, all of these nickel(0) derivatives show enhanced intramolecular silyl group exchange between the nitrogen and oxygen centers, due to the proximity of the nitrogen lone pair of the  $\text{C}=\text{NSi}$  group to the transannular  $\text{O}-\text{Si}$  moiety in the 10-membered chelate ring.

Further work from our laboratory on this ligand rearrangement will be focused on the mechanism of formation of these products.

**Acknowledgment.** This work was supported by the Natural Sciences and Engineering Research Council of Canada. We gratefully acknowledge Professor James Trotter for the use of his X-ray diffractometer and structure solving programs. We also thank the NMR staff at Simon Fraser University for running  $^{15}\text{N}$  and  $^{29}\text{Si}$  spectra.

**Registry No.** **8**, 92097-62-6; **9**, 92097-63-7; **10**, 92097-61-5; **11**, 92097-65-9; **12**, 92097-64-8; **15**, 92097-66-0;  $[\text{Ni}(\text{CH}_3)\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$ , 81603-07-8;  $[\text{Ni}(\eta^1\text{-CH}=\text{CH}_2)\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$ , 81610-99-3;  $[\text{Ni}(\eta^1\text{-CH}_2\text{CH}=\text{CH}_2)\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$ , 81603-08-9;  $[\text{Ni}(\text{Ph})\text{N}(\text{SiMe}_2\text{CH}_2\text{PPh}_2)_2]$ , 81603-09-0.

**Supplementary Material Available:** Tables of calculated hydrogen coordinates and isotropic thermal parameters (Table VI), final anisotropic thermal parameters (Table VII), torsion angles (Table VIII), and observed and calculated structure factors (Table IX) (27 pages). Ordering information is given on any current masthead page.

(23) Klebe, J. J. *Am. Chem. Soc.* **1968**, *90*, 5246-5251.